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"A METHOD OF MAKING BROMIDE OR IODIDE ION SENSITIVE ELECTRODES"

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH Rafi Marg, New Delhi-110001,
India, an Indian registered body incorporated under the Registration of
Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

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This invention is conceived by Gollakota Prabhakara Rao, Navin Chandra and Ganesa Ganapadigal Subramanian, all scientists of Central Electrochemical Research Institute, Karaikudi and Indian citizens and relates to ^a~~the~~ method of making bromide ^Nand iodide sensitive ~~membrane~~ electrodes (ISE) ~~and the structure made thereby~~

The concentration of bromide ^{or} and iodide ions in solutions has hitherto been estimated using a number of analytical methods including electro analytical methods such as potentiometry using electrodes of second kind viz. Ag/AgBr or Ag/ AgI electrodes. The conventional methods of analysis are time consuming. The Ag/AgBr and Ag/AgI electrodes are adversely affected in the presence of redox species particularly oxidizing agents present as constituent or impurity in solution and are also photosensitive and fragile. In recent years bromide ^{or} and iodide ion sensitive electrodes which are sturdy and insensitive to the presence of redox species in solutions have been reported in literature for the direct determination of bromide and iodide ions in solution. The preparation of these electrodes involves making of suitable membranes sensitive to ions to be estimated in solution from a composite of inorganic salts and constructing electrode using such membranes. However, neither the actual details the preparation and composition of the membranes nor the conventional details of these electrodes are fully described in literature.

The object of the present invention is to work out the details of the procedure for making bromide ^{or} and iodide sensitive membranes and to develop bromide and iodide sensitive electrodes making use

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of the membranes so prepared that would give steady and stable potentials in solution containing bromide/iodide ions.

To these ends the invention broadly consists of working out the details of the preparation of the Br^- / I^- ion sensitive membranes and the procedure of constructing ion sensitive membrane electrodes using such membranes.

The preparation of $\text{Ag}_2\text{S}=\text{AgBr}$ and $\text{Ag}_2\text{S}=\text{AgI}$ composite, used as active material for Br^- and I^- ISEs respectively, involves precipitation by addition of appropriate quantity of AgNO_3 to a mixture of appropriate quantities of $\text{Na}_2\text{S}=\text{NaBr} / \text{Na}_2\text{S}=\text{NaI}$. The precipitates are digested, washed, filtered, dried and powdered to a particle size of about 75 microns.

In the next step, a sample of the active material is compressed in a die under vacuum to obtain a mechanically stable and substantially impervious membrane.

The membranes obtained by above procedure are either mounted in hollow cylindrical glass/PVC tubes by fixing them to one end of the tube of an epoxy or moulded using a suitable plastic. A shielded wire is fixed to the inner surface of the membrane with help of the conducting epoxy prior to incorporating it in the electrode body.

The potential of the Ion Sensitive Electrodes so constructed is recorded against a double junction reference electrode such as Ag/AgCl electrode using a high input impedance pH/ millivoltmeter (sensitivity ± 0.1 mV) in solutions containing test ions (Br^- or I^- ions) in the background of an inert electrolyte.

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The I=ISE is sensitive to cyanide and mercury ions also and the response of I=ISE was recorded seperately in these solutions also.

Dated this 29th day of August 1985

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COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

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COMPLETE SPECIFICATION

(Section-10)

"A METHOD OF MAKING BROMIDE OR IODIDE ION SENSITIVE ELECTRODES"

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH Rafi Marg, New Delhi-110001,
India, an Indian registered body incorporated under the Registration of
Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention
and the manner in which it is to be performed :—

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This is an invention by Gollakota Prabhakara Rao, Navin Chandra and Ganesa Ganapadigal Subramanian, all of Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India, all Indian citizens and relates to a method of making bromide or iodide ion sensitive electrodes.

The bromide and iodide ion-sensitive electrode, produced by the method of this invention is useful for the estimation of concentration of the respective ion in solution. This electrode have got varied applications. For example, the bromide ion-sensitive electrode can be used for the determination of concentration of cetyl trimethyl ammonium bromide (a surfactant) used in metal finishing baths. Similarly, iodide ion sensitive electrode is useful for estimation of iodide ion concentration in the process chemical industries. Iodide electrode is also sensitive to mercury and cyanide ions in solution. Hence in the absence of iodide and cyanide, mercury and in the absence of iodide and mercury, cyanide ion concentration in solution can also be estimated using this electrode. This electrode is, thus, very useful for pollution monitoring purposes.

The concentration of bromide or iodide ion in solutions has hitherto been estimated using a number of analytical methods such as potentiometry using electrodes of second kind viz. Ag/AgBr or Ag/ AgI). These electrodes are, however, adversely affected in the presence of oxidizing agents present as impurity in solution and are fragile. The conventional methods of analysis (e.g. titrimetry) are time consuming and can not go down to the detection limits achieved by the ion sensitive electrodes of the

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present invention. The bromide and iodide ion sensitive electrodes for the direct determination of bromide and iodide ions in solution, which are sturdy and insensitive to oxidizing species present in solution, have been reported in literature in recent years. The preparation of this electrode involves making of suitable membranes, sensitive to ions to be estimated in solution, from a composite of inorganic salts and constructing electrode using such membranes.

The object of the present invention is to provide a process for making bromide and iodide sensitive membranes and also to provide a process for making bromide and iodide ion sensitive electrode making use of the membranes. The membranes so prepared would give steady and stable potentials in solution containing bromide/iodide ions.

According to this invention, there is provided a method of making bromide or iodide ion sensitive electrode which comprises preparing a composite of Ag Br and Ag_2S in the case of bromide ion sensitive electrodes and AgI and Ag_2S in the case of iodide ion sensitive electrodes by adding AgNO_3 to a slight excess of mixture of the Na_2S and NaBr or NaI, digesting the resulting precipitate and washing the precipitate thoroughly with water and/or acetone slurring the digested precipitate with carbon disulphide, washing the slurry formed with water, drying and powdering the resultant product compressing the powder under vacuum to obtain non-porous membrane, incorporating the membrane into an electrode body using a epoxy sealant after fixing a

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shielded wire contact lead to the inner surface of the membrane with the help of a conductive epoxy material.

The preparation of $\text{Ag}_2\text{S-AgBr}$ and $\text{Ag}_2\text{S-AgI}$ composite, used as active material for Br^- and I^- ISEs respectively, involves precipitation by addition of appropriate quantity of AgNO_3 to a mixture of appropriate quantities of $\text{Na}_2\text{S-NaBr}$ / $\text{Na}_2\text{S-NaI}$. The composition of $\text{Na}_2\text{S-NaBr}$ / $\text{Na}_2\text{S-NaI}$ mixtures is so chosen that the precipitate contains 30 to 70 mole percent of Ag_2S . The precipitates are digested, washed, filtered, dried and powdered to a particle size of about 75 microns.

In the next step, a sample of the active material (about 1-3 gms) is compressed for 5-10 minutes at 6-8 tons/cm² pressure in a die under vacuum to obtain a mechanically stable and substantially impervious membrane of 13 mm diameter and 2-3 mm thickness.

The membranes obtained by the above procedure were either mounted in hollow cylindrical glass/PVC tubes by fixing them to one end of the tube with the help of an epoxy or moulded using a suitable plastic. A shielded wire is fixed to the inner surface of the membrane with the help of the conducting epoxy prior to incorporating it in the electrode body.

The potential of the Ion Sensitive Electrodes so constructed was recorded against a double junction reference electrode such as Ag/AgCl electrode using a high input impedance PH/milli-voltmeter (sensitivity ± 0.1 mV) in solutions containing test ions (Br⁻ or I⁻ ions) in the background of an inert electrolyte. The I⁻ISE is sensitive to cyanide and mercury ions also and the response of I⁻ISE was recorded separately in these solutions also.

The potential (E) of the electrodes, when plotted versus the logarithm of the concentration (C) of the test ion in solution gave a straight line.

Example-I

The Br⁻ISE based on Ag₂S-AgBr composite membrane was prepared following the procedure given below:

A composite of 1:1 mole ratio AgBr-Ag₂S was prepared by adding AgNO₃ to a slight excess of a mixture of appropriate quantities of Na₂S and NaBr. The precipitate formed was digested and washed

thoroughly with water followed by acetone. After slurring with carbon disulphide the precipitate was again washed thoroughly with water followed by acetone and dried at 80°C. The dried precipitate was powdered to a particle size of about 75 micron. 1.5 gms of the powdered sample was compressed at 7 tons/cm² pressure for 10 minutes under vacuum to obtain a substantially non-porous membrane of 13 mm diameter, Part No.1 in Fig.1 of the drawing accompanying this specification which represents the schematic diagram of the electrode of the present invention. The membrane was incorporated in a glass electrode body (4) using an epoxy sealant after fixing a shielded wire contact lead, (2) to the inner surface of the membrane with the help of a conducting epoxy (3).

The response of the above electrode was evaluated in NaBr solutions (in 1.0 M NaNO₃ background) by measuring the potential of the electrode against a double junction Ag/AgCl reference electrode. The results are given below in Table-I.

TABLE-1

Concentration of Br ⁻ (M) in solution	Potential versus Ag/AgCl (mV)
10 ⁻¹	-66.7
10 ⁻²	- 9.5
10 ⁻³	47.4
10 ⁻⁴	104.2
10 ⁻⁵	160.1
10 ⁻⁶	201.3

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Example II

Another electrode based on Ag_2S - AgBr composite membrane was prepared by following procedure:

Ag_2S - AgBr composite containing 40 mole percent Ag_2S was precipitated by adding AgNO_3 to a slight excess of a mixture of appropriate quantities of Na_2S and NaBr .

The precipitate was digested with water several times and then washed with acetone. After slurring with carbon disulphide the precipitate was again washed with water followed by acetone and dried at 80°C . The dried composite was powdered to about 75 micron particle size. 1.8 gms of the powdered sample was compressed at 7 ton/cm^2 pressure for 10 minutes under vacuum to obtain a substantially non-porous membrane of 13 mm diameter (1). After providing the inner contact lead (2) with the help of a conducting epoxy (3) the membrane was moulded in A.B.S. plastic body (4).

The response of the above electrode was recorded in NaBr solutions in the background of 1.0 M NaNO_3 by measuring the potential of the electrode against a double junction Ag/AgCl

reference electrode. The results are given below in Table-II.

TABLE-II

Concentration of Br^- (M) in solution	Potential versus Ag/AgCl (mV)
10 ⁻¹	-63.4
10 ⁻²	- 6.6
10 ⁻³	51.8
10 ⁻⁴	108.0
10 ⁻⁵	164.2
10 ⁻⁶	204.8

Example-III

An Ag_2S -AgI composite membrane based Ion Sensitive Electrode was prepared by following procedure.

^{1:1}
~~1:1~~ mole ratio Ag_2S -AgI composite was prepared by slowly adding AgNO_3 to a slight excess of a mixture of Na_2S -NaI. The precipitate was digested with water and washed thoroughly with water followed by acetone. After slurring with carbon disulphide the precipitate was again washed with water followed by acetone. The precipitate was then dried at 80°C and powdered to about 75 micron size. 1.5 gms of the precipitate were compressed at 7.0 tons/cm² under vacuum for 10 minutes to obtain a substantially non-porous membrane of 13mm diameter (1). After fixing a shielded cable (2) to the inner surface of the membrane with the help of a conducting epoxy (3) the membrane was moulded in A.B.S. plastic body (4).

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The response of the electrode was evaluated in KI solutions in 1.0 M NaNO_3 background by measuring its potential against a double junction Ag/AgCl reference electrode on a digital pH/mV meter. The results are given below in Table-III.

TABLE-III

Concentration of Br^- (M) in solution	Potential versus Ag/AgCl (mV)
10^{-1}	-311.2
10^{-2}	-254.2
10^{-3}	-195.6
10^{-4}	-136.9
10^{-5}	- 80.0
10^{-6}	- 21.9
10^{-7}	24.9

The I^- electrode is sensitive to CN^- and mercury ions also in solution. The response of the electrode was measured in NaCN solutions in 0.10M KOH background and $\text{Hg}(\text{NO}_3)_2$ solutions in 0.10M NaNO_3 background. The results are given in Table-IV and V respectively.

TABLE-IV

Concn. of CN^- ions (M)	Potential versus Ag/AgCl electrode (mV)
10^{-2}	-240.0
10^{-3}	-178.4
10^{-4}	-116.7
10^{-5}	- 58.6
10^{-6}	- 23.8

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TABLE-V

Concn. of Hg^{2+} ions (M)	Potential versus Ag/AgCl electrode (mV)
10^{-3}	426.8
10^{-4}	367.0
10^{-5}	305.8
10^{-6}	251.9
10^{-7}	220.7

EXAMPLE-IV

Another Ag_2S -AgI composite based membrane electrode was prepared as follows:

1:1 mole ratio Ag_2S - AgI composite was precipitated by adding AgNO_3 to a slight excess of a mixture of appropriate quantities of Na_2S + NaI. The precipitate was digested, washed with water followed by acetone, slurried with carbon disulphide and again washed thoroughly with water followed by acetone and dried at 80°C . After powdering to about 75 micron size, 1.8 gms of the precipitate were compressed at 8.0 tons/cm^2 pressure for 10 minutes under vacuum to obtain a substantially non-porous membrane of 13mm diameter (1). The membrane was fixed to one end of a PVC tube (4) with the help of an epoxy binder after providing contact lead wire (2) to the inner surface of the membrane with the help of silver epoxy (3).

The response of the membrane was evaluated in KI solutions in 1.0M NaNO_3 background by measuring its potential against a double junction Ag/AgCl reference electrode. The results are given in Table-VI.

TABLE-VIII

Concn.of Hg^{2+} ions (M)	Potential versus Ag/AgCl electrode (mV)
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10^{-3}	418.3
10^{-4}	359.4
10^{-5}	300.3
10^{-6}	242.3
10^{-7}	209.0

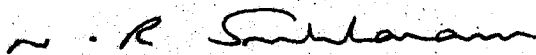
It is clear from the data presented in Tables I to VIII that the Br^- ISE, responds to concentration of Br^- ions in solution and I^- IE responds to I^- , CN^- and Hg^{2+} ions in solution. Plot of potential of the ISE's versus concentration of that of ions is shown in Fig.2. The reproducibility of the potential data for a given electrode is better than ± 0.5 millivolts.

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WE CLAIM

1. A method of making bromide or iodide ion sensitive electrode which comprises preparing a composite of Ag Br and Ag₂S in the case of bromide ion sensitive electrodes or AgI and Ag₂S in the case of iodide ion sensitive electrodes by adding AgNO₃ to a slight excess of mixture of the Na₂S and NaBr or NaI, digesting the resulting precipitate and washing the precipitate thoroughly with water and/or acetone slurring the digested precipitate with carbon disulphide washing the slurry formed with water, drying and powdering the resultant product compressing the powder under vacuum to obtain non-porous membrane, incorporating the membrane into an electrode body using a epoxy sealant after fixing a shielded wire contact lead to the inner surface of the membrane with the help of a conductive epoxy material.
2. A method as claimed in claim 1 wherein the precipitate obtained is dried at 80°C.
3. A method as claimed in claims 1 and 2 wherein the dried precipitate is powdered to about 75 micron particle size.
4. A method as claimed in claims 1-3 wherein the powdered precipitate is compressed at 7 ton/cm² pressure for 10 minutes under vacuum.
5. A method of making a bromide or iodide ion sensitive electrode substantially as herein described with reference to the examples.

Dated this 3rd day of October 1986



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APP NO. ~~781/1978~~ 164565

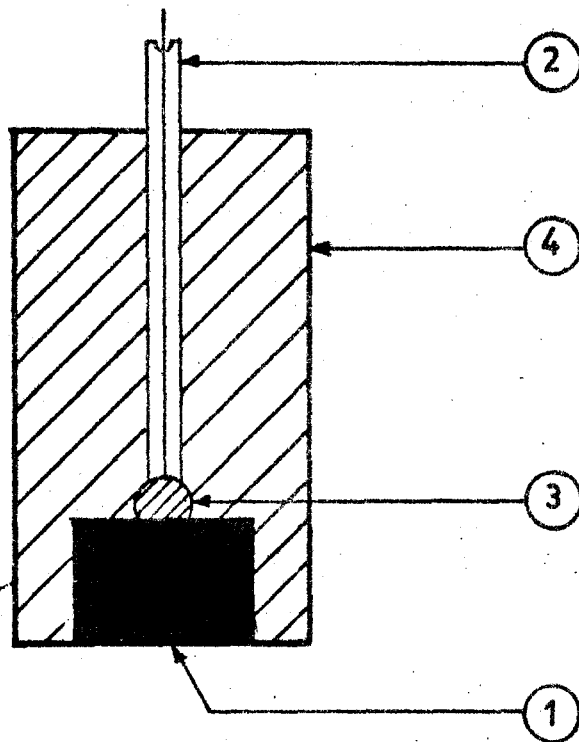


FIG. 1

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WE CLAIM

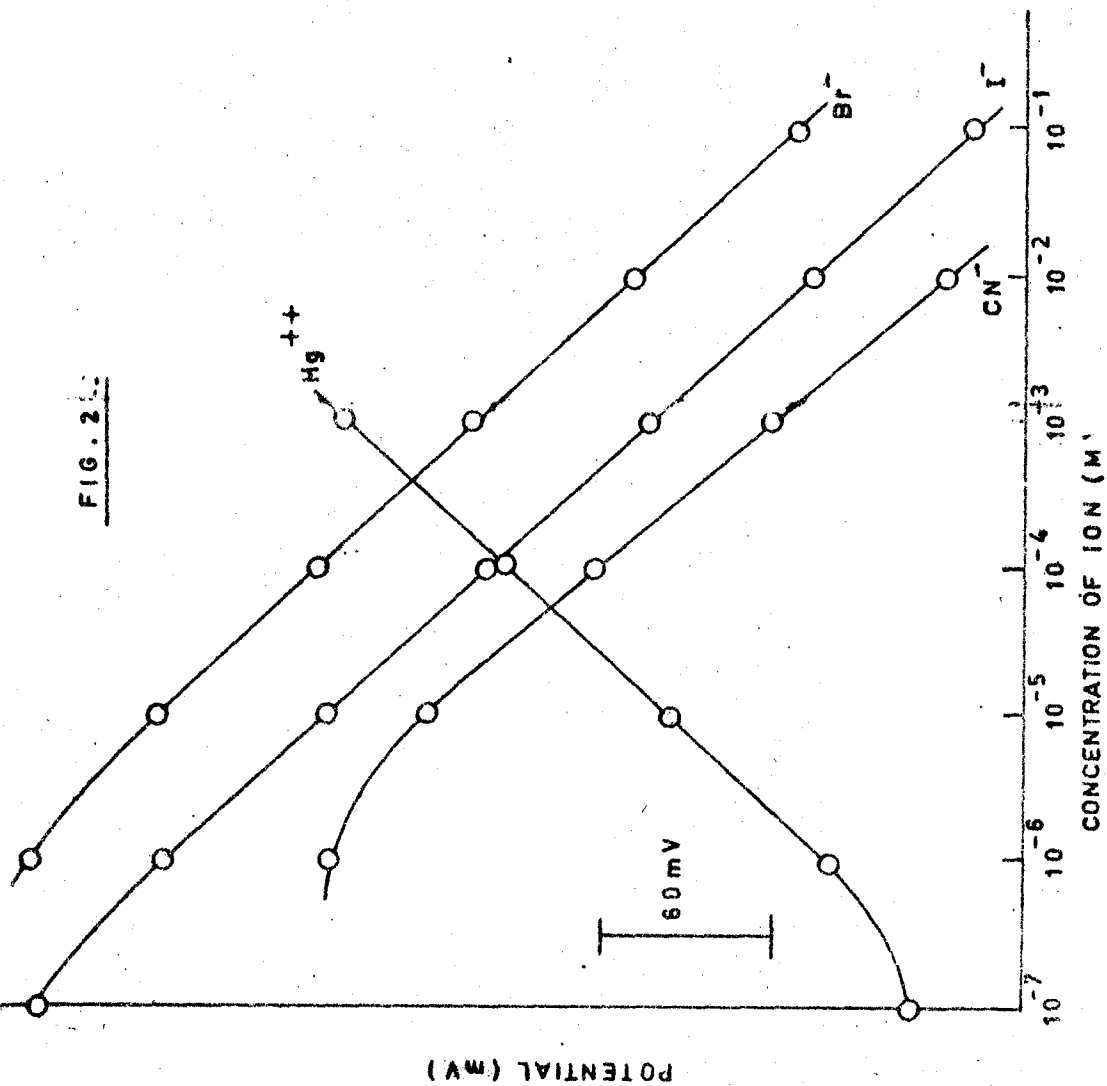
1. A method of making bromide or iodide ion sensitive electrode which comprises preparing a composite of Ag Br and Ag₂S in the case of bromide ion sensitive electrodes or AgI and Ag₂S in the case of iodide ion sensitive electrodes by adding AgNO₃ to a slight excess of mixture of the Na₂S and NaBr or NaI, digesting the resulting precipitate and washing the precipitate thoroughly with water and/or acetone slurring the digested precipitate with carbon disulphide washing the slurry formed with water, drying and powdering the resultant product compressing the powder under vacuum to obtain non-porous membrane, incorporating the membrane into an electrode body using a epoxy sealant after fixing a shielded wire contact lead to the inner surface of the membrane with the help of a conductive epoxy material.
2. A method as claimed in claim 1 wherein the precipitate obtained is dried at 80°C.
3. A method as claimed in claims 1 and 2 wherein the dried precipitate is powdered to about 75 micron particle size.
4. A method as claimed in claims 1-3 wherein the powdered precipitate is compressed at 7 ton/cm² pressure for 10 minutes under vacuum.
5. A method of making a bromide or iodide ion sensitive electrode substantially as herein described with reference to the examples.

Dated this 3rd day of October 1986

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FIG. 2



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